

# Melting of alloys along grain boundaries

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We discuss melting of alloys along grain boundaries as a free boundary problem for two moving solid-liquid interfaces. One of them is the melting front and the other is the solidification front. The presence of the triple junction plays an important role in controlling the velocity of this process. The interfaces strongly interact via the diffusion field in the thin liquid layer between them. In the liquid film migration (LFM) mechanism the system chooses a more efficient kinetic path, which is controlled by diffusion in the liquid film on relatively short distances. However, only weak coherency strain energy is the effective driving force for LFM in the case of melting of one-phase alloys. The process with only one melting front would be controlled by the very slow diffusion in the mother solid phase on relatively large distances.

## I. INTRODUCTION

In our previous paper [1] we discuss partial melting of the binary alloys which proceeds via the liquid film migration (LFM) mechanism. The liquid phase separates two nearly parabolic fronts (see Fig. 1). If only the melting front existed, the process would be controlled by the very slow diffusion in the mother solid phase. In the LFM mechanism the system chooses a more efficient kinetic path which is controlled by much faster diffusion in the liquid film. However, in this case the relatively weak coherency strain energy is involved as an effective driving force for this process.

The early observations of liquid film migration (LFM) were made during sintering in the presence of liquid phase [2] or during partial melting of alloys [3] (see [4] for a review). Nowadays LFM is a well established phenomenon of great practical importance. In LFM one crystal is melting and another one is solidifying. Both solid-liquid interfaces move together with the same velocity. The migration velocity is much smaller than the characteristic velocity of atomic kinetics at the interfaces. Therefore, both solids should at the interfaces be locally in thermodynamic equilibrium with the liquid phase. On the other hand, these local equilibrium states should be different for the two interfaces to provide the driving force

for the process. It is by now well accepted (see, for example, [4, 5]) that the difference of the equilibrium states at the melting and solidification fronts is due to the coherency strain energy, important only at the melting front because of the sharp concentration profile ahead the moving melting front (diffusion in the solid phase is very slow and the corresponding diffusion length is very small). The solute atoms diffuse ahead of the moving film and the coherency strain energy in such frontal diffusion zone arises from the solute misfit. Thus, the equilibrium liquid composition at the melting front, which depends on the coherency strain energy and on the curvature of the front, differs from the liquid composition at the unstressed and curved solidification front. This leads to the necessary gradient of the concentration across the liquid film and the process is controlled by the diffusion in the film.

Thus, a theoretical description of LFM requires the solution of a free boundary problem for two combined moving solid-liquid interfaces with a liquid film in between. In Ref.[6] this problem was considered for simplified boundary conditions: the temperature and the chemical composition along each interface were kept constant. This means that any capillary, kinetic and crystallographic effects at the interfaces were neglected. It was found that under these simplified boundary conditions two co-focal parabolic fronts can move together with the same velocity. The situation is rather similar to a steady-state motion of one parabolic solidification front into a supercooled melt or one parabolic melting front into a superheated solid. In this approximation the Peclet numbers were found, but the steady-state velocity remained undetermined at that stage. Thus, the problem of velocity selection arises.

Solvability theory has been very successful in predicting certain properties of pattern selecting in dendritic growth and a number of related phenomena (see, for example, [7, 8, 9]). We note that capillarity is a singular perturbation and the anisotropy of the surface energy is a prerequisite for the existence of the solution in this theory. In [1] we extended the selection theory for the process of liquid film migration where the strong diffusion interaction between melting and solidification fronts

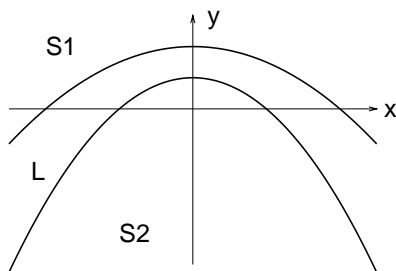


FIG. 1: Schematic representation of two moving nearly parabolic fronts discussed in Ref. [1];  $S1$  and  $S2$  are the melting and growing solids, and  $L$  is the liquid film.

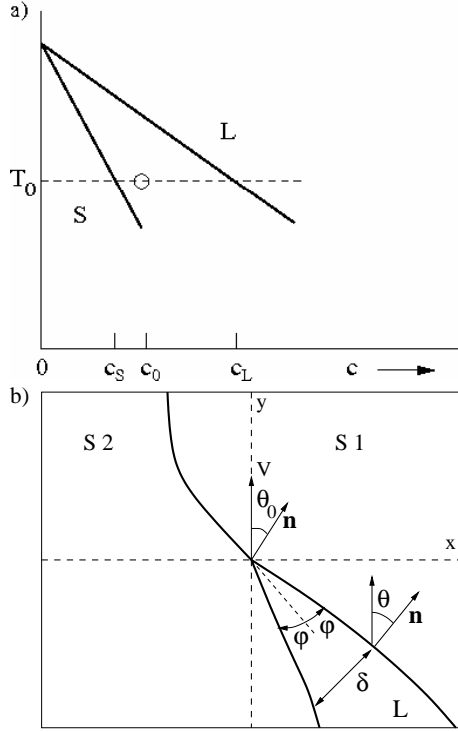


FIG. 2: Schematic representation of the phase diagram a) and configuration of different interfaces near the triple junction b). This structure moves steadily with the velocity  $V$  in the vertical  $y$  direction. The triple junction is located at the origin. Above the origin two solid grains  $S1$  and  $S2$  are separated by the grain boundary. Below the origin two grains are separated by the thin liquid layer  $L$ .

plays a crucial role.

The nucleation of the melt often takes place at the grain boundaries of the mother solid phase. Then the thin liquid layer extends along the grain boundary. In the present paper we discuss the liquid film migration during the partial melting along the grain boundary (see Fig.2). The presence of the triple junction in this geometry drastically changes the structure of the theory. It produces a very strong perturbation of the solid-liquid interface and the anisotropy of the surface tension does not play an important role in such processes [10, 11, 12].

## II. FORMULATION OF THE PROBLEM

We discuss the two-dimensional problem of the steady-state motion of a thin liquid film during the process of isothermal melting of a binary alloy along the grain boundary. The schematic phase diagram of the binary alloy and the geometry of the process are presented in Fig.2. We note that the discussed geometry corresponds to the spontaneous breaking of the reflection symmetry  $x \rightarrow -x$ . The equivalent structure can be obtained by the reflection  $x \rightarrow -x$  of the structure presented in Fig.2b.

We assume that the diffusion in the solid phases is very slow and the concentration  $c$  in the liquid film obeys the Laplace equation. We introduce the normalized concentration  $C = (c - c_L)/(c_L - c_S)$  with  $c_L$  and  $c_S$  being the liquidus and solidus concentrations of the equilibrium phase diagram at a given temperature,  $T_0$ . Then the equilibrium concentration and the mass balance conditions at the solidification front, which separates the grain  $S2$  and the liquid phase, read

$$C_2 = -d_0 K_2, \quad V_n = -D \partial C / \partial \mathbf{n}. \quad (1)$$

At the melting front, which separates the grain  $S1$  and the liquid phase, the equilibrium concentration is changed by the presence of the elastic coherency strain energy [4] and also the diffusional flux changes because in the solid ahead of the melting front the concentration is  $c_0$  which is different from  $c_S$ :

$$C_1 = -b \Delta^2 + d_0 K_1, \quad V_n (1 - \Delta) = -D \partial C / \partial \mathbf{n}. \quad (2)$$

Here  $V_n$  is the normal velocity;  $D$  is the diffusion coefficient in the liquid film;  $K$  is the curvature assumed to be positive for the interfaces in Fig.1;  $\Delta = (c_0 - c_S)/(c_L - c_S)$  is the dimensionless driving force;  $b = Y \Omega (da/dc)^2 / a^2 f_L''$  is the dimensionless constant which describes the coherency strain energy [5],  $\Omega$  is the atomic volume,  $Y$  is the bulk elastic modulus,  $a$  is the atomic constant,  $f_L(c)$  is the free energy of the liquid phase per atom,  $f_L''$  is the second derivative of  $f_L(c)$  at  $c = c_L$ ;  $d_0$  is the chemical capillary length which is assumed to be isotropic in the present problem,  $d_0 = \gamma \Omega / f_L''(c_L - c_S)^2$  where  $\gamma$  is the surface energy of the solid-liquid interface.

At an arbitrary rotation of the grain boundary (Fig. 2) the angle between fronts at the triple junction  $2\varphi$  remains unchanged,  $\cos \varphi = \gamma_b / 2\gamma$ , where  $\gamma_b$  is the surface tension of the grain boundary. This additional thermodynamical condition eventually allows to find a unique solution for the whole structure and the velocity of steady-state propagation of this structure.

In the general case, the formulated problem is quite complicated because two fronts interact non-locally through the diffusion field inside of the liquid phase. At small driving forces  $\Delta$  and small angles  $2\varphi$  between fronts this problem can be treated in the so-called ‘‘lubrication’’ approximation which is also called the boundary layer model (BLM) in the context of solidification. This allows to reduce the original nonlocal problem to the system of ordinary differential equations for the shapes of the fronts.

## III. LUBRICATION APPROXIMATION

The crucial ingredient of the lubrication approximation is that the variation of the concentration field in the thin liquid layer in the direction normal to the interfaces is much larger than in the tangential direction. In this approximation the two fronts are close to each other and

they can be parametrized by two functions which are invariant to the transformation of the coordinate system:  $K(\theta)$  and  $\delta(\theta)$ .  $K$  is the curvature of one of the interfaces and  $\delta$  is the distance between the interfaces in the normal direction;  $\theta$  is the angle between the normal to one of interfaces  $\mathbf{n}$  and the direction of the steady-state growth (see Fig.2) Alternatively, one can use functions  $\theta(s)$  and  $\delta(s)$  where  $s$  is the arc-length along the interface and  $K = \partial\theta/\partial s$ . The lubrication approximation is valid if

$$K\delta \ll 1$$

which is the small parameter of the theory. We will see later that this condition is fulfilled if  $\Delta$  and  $\varphi$  are small.

Let us derive the equations for the solidification and melting fronts using basic Eqs. (1, 2) and the crucial ingredient of the lubrication approximation that the concentration field varies linearly in the normal direction. Then in the main approximation  $\partial C/\partial \mathbf{n} \approx (C_1 - C_2)/\delta$  and from the mass balance condition, Eq. (1) we find

$$V \cos \theta = D \frac{b\Delta^2 - 2d_0K}{\delta}, \quad (3)$$

where  $V$  is the steady-state velocity and we have already used the fact that the interfaces are close to each other:  $K_1 \approx K_2 = K$ . The derivation of the second equation is slightly more delicate, because if one takes the difference between two mass balance conditions all remaining terms are small and one should take into account the small differences between normal velocities and normal gradients at two interfaces:

$$V_{n1} - V_{n2} + D \left[ \left( \frac{\partial C}{\partial \mathbf{n}} \right)_1 - \left( \frac{\partial C}{\partial \mathbf{n}} \right)_2 \right] = V \Delta \cos \theta. \quad (4)$$

Evaluating the term in the right-hand-side which is already proportional to the small parameter  $\Delta$  we have ignored the difference between normal velocities at two interfaces. In the left-hand-side, the small difference in normal velocities is due to the differences in the normal directions at the two interfaces:

$$(V_{n1} - V_{n2}) \approx V \sin \theta \partial \delta / \partial s = V K \sin \theta \partial \delta / \partial \theta. \quad (5)$$

The small difference in normal gradients at the two interfaces is due to the curvature of the interface. The simple way to see this effect is to look for the solution of the Laplace equation for the concentration field  $C = A + B \ln r$  in the local polar coordinate system rather than in the Cartesian coordinates as it would be convenient for flat interfaces. One of the interfaces is located at  $r = 1/K(\theta)$  and the other is at  $r = (1 + K\delta)/K$ . Then using the fact that the gradient scales as  $1/r$  and  $K\delta \ll 1$  we obtain:

$$D \left[ \left( \frac{\partial C}{\partial \mathbf{n}} \right)_1 - \left( \frac{\partial C}{\partial \mathbf{n}} \right)_2 \right] \approx -D \left( \frac{\partial C}{\partial \mathbf{n}} \right) K\delta = V K \delta \cos \theta. \quad (6)$$

Inserting Eqs. (5, 6) into Eq. (4) we obtain:

$$\frac{\partial}{\partial s} [\delta \sin \theta] = K \frac{\partial}{\partial \theta} [\delta \sin \theta] = \Delta \cos \theta. \quad (7)$$

Eqs. (3) and (7) are the desired equations in the leading order of the lubrication approximation. As seen from Eq.(7)  $K\delta \sim \Delta \ll 1$  which justifies the approximation used in the limit of small driving forces.

At the triple junction, where  $\delta = 0$  and  $\partial \delta / \partial s = 2\varphi$ , Eq. (7) reads:

$$\tan \theta_0 = \frac{\Delta}{2\varphi}, \quad (8)$$

where  $\theta_0$  is the value of  $\theta$  at the triple junction. The grain boundary is rotated by approximately the same angle  $\theta_0$  at the triple junction (see Fig. 2). One can eliminate the curvature  $K$  from Eqs. (3, 7) and obtain the closed first order differential equation for the function  $\delta(\theta)$ :

$$\frac{\partial}{\partial \theta} [H(\theta) \sin \theta] = \frac{\cos \theta}{1 - \nu H(\theta) \cos \theta}, \quad (9)$$

where we have introduced the rescaled quantities:

$$H = \frac{\delta b \Delta}{2d_0}, \quad \nu = \frac{2Vd_0}{Db^2\Delta^3}. \quad (10)$$

We should find the smooth solution of this equation which starts from  $H = 0$  at  $\theta = \theta_0$  and diverges as  $H \rightarrow 1/(\nu \cos \theta)$  when  $\theta \rightarrow \pi/2$ . It turns out that this is an eigenvalue problem and such a solution exists only for specific values of the eigenvalue parameter  $\nu$  which depends only on  $\theta_0$ . Using Eqs. (8, 10) we can present the final result for the steady-state growth velocity  $V$  in the form:

$$V = \frac{Db^2\Delta^3}{2d_0} \nu(\Delta/2\varphi), \quad (11)$$

where the scaling function  $\nu(\Delta/2\varphi)$ , obtained by the numerical solution of Eq. (9), is presented in Fig. 3 and has the following asymptotic behavior:

$$\nu(\Delta/2\varphi) \approx 0.25, \quad \Delta/\varphi \ll 1 \quad (12)$$

and

$$\nu(\Delta/2\varphi) \approx 2.12(\Delta/2\varphi)^3, \quad \Delta/\varphi \gg 1 \quad (13)$$

Eqs. (11), (12) and (13) are the main results of this paper providing the expression for the steady-state velocity  $V$  of the melting process along the grain boundary in terms of the driving force  $\Delta$  and material parameters.

The analysis of this section is close in spirit to the analysis given in Ref. [12] where we discussed the melting process in eutectic and peritectic systems. However, apart from very different physical ingredients involved, the lubrication approximations used are quite different in these two cases. In Ref. [12] the assumption of small

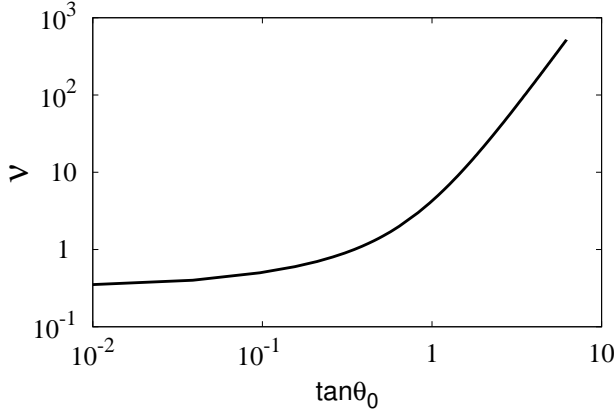


FIG. 3: The scaling function  $\nu$  vs.  $\tan \theta_0 = \Delta/2\varphi$ .

opening angles  $\varphi$  immediately leads to small variations of the angle  $\theta$  in the vicinity of the value  $\pi/2$ . In the present analysis, the additional small parameter  $\Delta$  leads to wide variations of the angle  $\theta$  depending on the ratio  $\Delta/\varphi$ , Eq. (8). Thus, the lubrication approximation developed here is more general than the approximation in Ref. [12]. It involves calculations of the whole scaling function  $\nu(\theta_0)$ , while in [12] only a single eigenvalue parameter was calculated. Of course, in the limit  $\theta_0 \rightarrow \pi/2$  the present problem can be mapped onto the problem of Ref. [12].

#### IV. KINETICS OF THE GRAIN BOUNDARY

The kinetics of the grain boundary plays an important role allowing the necessary rotation of the structure in the vicinity of the triple junction (Fig. 2). The angle  $\theta$  along the grain boundary should change from its value  $\theta_0$  at the triple junction to  $\pi/2$  far ahead of the junction. Moreover, the concentration at the grain boundary should change from its value  $c_S$  at the junction to the value  $c_0$  far ahead. The distribution of the concentration  $c$  in the grain boundary is given by the solution of the Chan equation, [13]:

$$D_b \delta_b \partial^2 c / \partial s^2 - (c - c_0) V \cos \theta = 0, \quad (14)$$

where  $D_b$  is the grain boundary diffusion coefficient,  $\delta_b$  is the thickness of the boundary, and  $s$  is arc-length;  $s = 0$  at the triple junction and  $s$  is negative along the grain boundary. It turns out that for small driving forces  $\Delta$  the characteristic length of the concentration decay is much shorter than the characteristic length for the shape changes. This allows to use the value  $\theta_0$  instead of the current values  $\theta(s)$ . Thus, we obtain:

$$c(s) - c_0 \approx (c_S - c_0) \exp(-k|s|),$$

$$k = \sqrt{V \cos \theta_0 / D_b \delta_b}. \quad (15)$$

The evolution of the grain boundary shape is controlled by the recrystallization kinetics [14]

$$V \cos \theta = V_b [-d_b K_b + b \Delta^2(s)], \quad (16)$$

where  $V$  is the steady-state velocity which we have already found from the analysis of the melting process;  $V_b$  is the characteristic velocity scale proportional the grain boundary mobility,  $d_b$  is the capillary length proportional to the surface tension of the boundary and  $K_b = \partial \theta / \partial s$  is the curvature. The last term in Eq. (16) is due to the coherency strain energy effects and  $\Delta(s) = [c(s) - c_0] / (c_L - c_S)$ , where  $c(s)$  is given by the distribution Eq. (15). Eq. (16) can be integrated once leading to:

$$\theta(s) - \theta_0 = -\frac{V x(s)}{V_b d_b} + \frac{b \Delta^2}{2 k d_b} [\exp(-2k|s|) - 1], \quad (17)$$

where  $x(s) = \int_0^s ds \cos \theta < 0$  (see Fig. 2b). Indeed, the characteristic length of the concentration decay scales as  $k^{-1} \sim 1/\sqrt{V}$  and it is much shorter than the characteristic length of the angle decay  $\theta(s)$  which scales as  $1/V$  (in the limit of small driving forces  $\Delta$ , the steady-state velocity  $V$  is also small according to Eq. (11)). We note also that the last term in Eq. (17), which is proportional to  $(D_b \Delta / D)^{1/2}$  ( $k d_b \sim (D / D_b)^{1/2} b \Delta^{3/2}$ ), is small in the limit of small driving forces  $\Delta$ . Thus, far ahead of the triple junction the position of the grain boundary relative to the junction is given by (see Fig. 2b):

$$x(-\infty) \approx -(\pi/2 - \theta_0) V_b d_b / V.$$

Moreover, the diffusional flux along the grain boundary has a nonzero value at the triple junction. In principal, this flux should be taken into account in the description of the diffusional field in the liquid phase. This effect has been neglected in the previous sections. More careful analysis shows that corrections to Eq. (3) and (7) due to this effect are small in the limit of small  $\Delta \ll 1$ . Thus, the grain boundary kinetics plays an important role in necessary adjustment of this interface but has no influence on the melting kinetics as we have already discussed previously in Ref. [12] in the context of the contact melting in eutectic and peritectic systems.

#### V. DISCUSSION

As we have already mentioned, the process with only one melting front (see Fig. 4a) would be controlled by the very slow diffusion in the mother solid phase. In this case the growth velocity scales as in the classical dendritic growth. Assuming that the diffusion coefficient in the solid phase  $D_s \ll D$ , we can present this scaling in the form [15]

$$V \sim \frac{D_s^2 \Delta^4}{D d_0} \alpha^{7/4}. \quad (18)$$

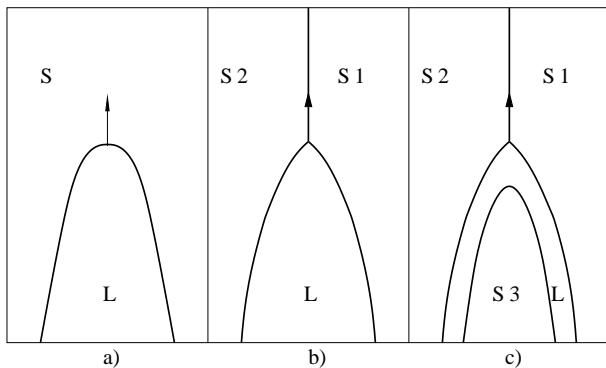


FIG. 4: Schematic representation of the symmetric melting structures. a)- with only one melting front during the process in bulk of the grain; b)- with only one melting front during the process along the grain boundary; c)- combined motion of the melting front along the grain boundary and the solidification front  $S3/L$  via the LFM mechanism.

This scaling involves the additional small parameter  $\alpha$  - the anisotropy of surface tension. For melting along the grain boundary, Fig. 4b, one should omit the anisotropy factor [11]:

$$V \sim \frac{D_s^2 \Delta^4}{D d_0}. \quad (19)$$

With the help of the LFM mechanism the system chooses a more efficient kinetic path to relax to the equilibrium state. For the case of two nearly parabolic fronts without grain boundary (see Fig.1), which was discussed in [1], the migration velocity scales as

$$V \sim \frac{D b^2 \Delta^3}{d_0} \alpha^{5/4}, \quad \Delta \ll \alpha^{1/2},$$

$$V \sim \frac{D b^2 \Delta^2}{d_0} \alpha^{7/4}, \quad \Delta \gg \alpha^{1/2}. \quad (20)$$

In the present paper we discuss melting along the grain boundary via the LFM mechanism (Fig. 2b). The nu-

cleation of the melt takes place at the grain boundaries of the mother solid phase. Then the thin liquid layer extends along the grain boundary. For small driving forces  $\Delta$  and for not too small angles  $\varphi$  the steady-state velocity of this process scales, according to Eq. (11), as

$$V \sim \frac{D b^2 \Delta^3}{d_0}. \quad (21)$$

If the nucleation of the melt takes place at the triple point where three grains meet together, the process could proceed as shown in Fig. 4c. This structure has not been investigated theoretically so far. However, we can guess that the velocity would scale as in Eq. (21). As we have already noted, the presence of the triple junction in this structure produces a very strong perturbation of the solid-liquid interface and the anisotropy of the surface tension does not play an important role in such processes. Thus, one can use the scaling given by the first relation in Eq. (20), which describes the structure in Fig.1, formally setting  $\alpha \sim 1$  [11]. We note that the velocities of different processes increase from Eq. (18) to Eq. (21).

Let us estimate the velocity  $V$  from Eq.(21) and the thickness of the film  $\delta \sim d_0/b\Delta$  from Eq.(10) using characteristic values of the parameters:  $D \sim 10^{-5} \text{cm}^2/\text{s}$ ,  $d_0 \sim 10^{-7} \text{cm}$ ,  $b \sim 0.05$  and  $\Delta \sim 0.05$ . This leads to  $V \sim 10^{-4} \text{cm/s}$  and  $\delta \sim 10^{-4} - 10^{-5} \text{cm}$ .

In conclusion, we have developed and analyzed a relatively simple model for the melting kinetics along the grain boundary in alloys. The process proceeds via LFM mechanism which is controlled by relatively fast diffusion in the liquid film. The presence of the triple junction plays an important role in controlling the velocity of this process. We solved this problem in lubrication approximation which allows to reduce the originally nonlocal problem to a local and analytically tractable problem. We derived the expression for the velocity of the melting process along the grain boundary in terms of the driving force and material parameters.

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- [1] Brener EA, Temkin DE. Phys Rev Lett 2005;94:184501
  - [2] Yoon DN, Hupmann WJ Acta Metall 1979;27: 973
  - [3] Muschik T, Kaysser WA, Hehenkamp T. Acta Metall 1989;37:603
  - [4] Yoon DN. Int. Mater. Rev 1995;40:149
  - [5] Yoon DN, Cahn JW, Handwerker CA, Blendell JE, Baik YJ. In: Interface Migration and Control of Microstructures. Am Soc. Metals. Park. Ohio 1985, p. 19.
  - [6] Temkin DE. Acta Mater 2005;53:2733
  - [7] Saito Y. Statistical Physics of Crystal Growth, World Scientific Publishing, Singapore, 1996.
  - [8] Kessler D, Koplik J, Levine H, Adv Phys 1988;37:255
  - [9] Brener EA, and Mel'nikov VI. Adv Phys 1991;40:53
  - [10] Temkin DE. Abstracts of ICASP, June 7-10 2005, Stockholm, Sweden (KTH, Stockholm, 2005)
  - [11] Brener EA, Huter C, Pilipenko D, Temkin DE. Phys Rev Lett 2007;99:105701
  - [12] Brener EA, Temkin DE. Acta Mater 2007;55:2785
  - [13] Cahn JW. Acta Metall 1959;7:18
  - [14] Brener EA, Temkin DE. Acta Mater 2002;50:1707
  - [15] Barbieri A, Langer JS. Phys Rev A 1989;39:5314